(Li-ion) batterijen & hun problemen

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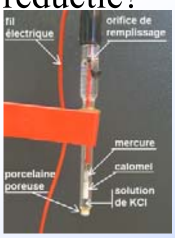
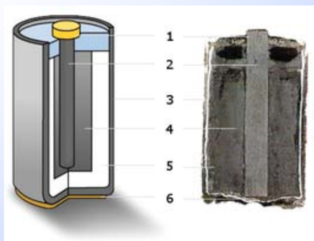
Batterijen

- Basis: Oxidatie aan ene kant, reductie aan andere kant
- Klassieke Zn batterij:
- Oxidatie $Zn+2NH_4Cl=ZnCl_2 + 2NH_3+H_2+2e$
- Reductie $2MnO_2 +H_2+ 2e=Mn_2O_3+ H_2 O$
- Potentiaal te berekenen uit reductiepotentialen: 1,5 V/cel
- Moeilijk omkeerbaar: reductie?
- Oorspronkelijke referentie van spanning met Hg
- +0,2444 V bij 25 °C





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Batterijen

Potentiaal te berekenen met Nernst potentialen (activiteiten≈concentraties)

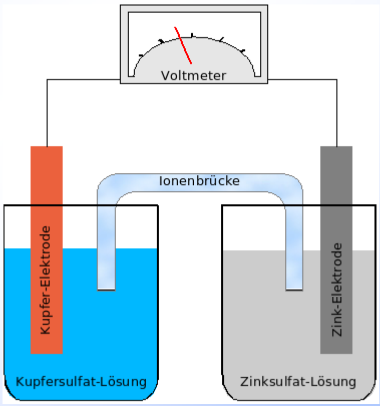
$$bB + cC \rightleftharpoons dD + eE$$

$$Q_a = \frac{\prod_j a_j^{\nu_j}}{\prod_i a_i^{\nu_i}} = \frac{a_B^b a_C^c}{a_D^d a_E^e} \quad Q_a \cong \frac{\prod_j [C]_j^{\nu_j}}{\prod_i [C]_i^{\nu_i}}$$

$$V \cong V_0 - \frac{RT}{nF}\ln(Q_a)$$

n = aantal electronen

F=96 485,3399 ± 0,0024 C · mol^{-1}



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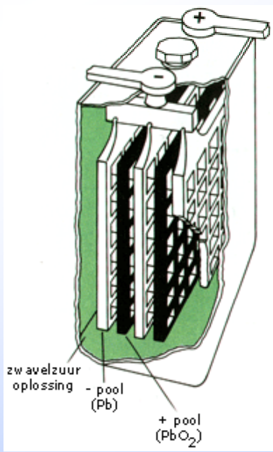
Batterijen

- Omkeerbare: voorbeeld loodaccu: ±2V/cel
- Oxidatie Pb + H_2SO_4=$PbSO_4$ + H_2+2e (ontploffingsgevaar zeker bij overladen, want dan hydrolyseert water in waterstof en zuurstof)
- Reductie PbO_2 + H_2 + 2e=PbO + H_2 O
-



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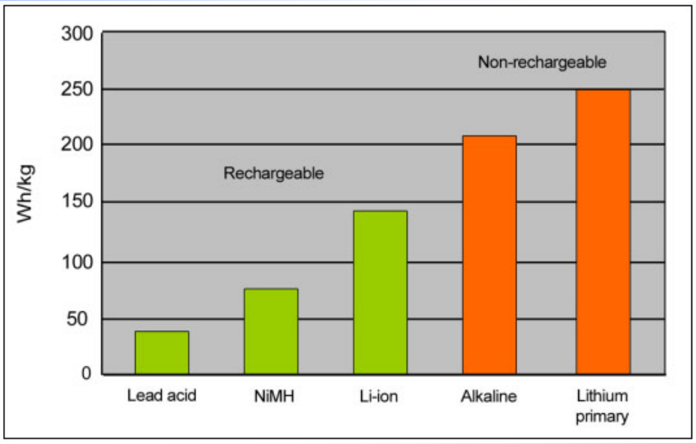
Waarom Li(-ion)?

- 

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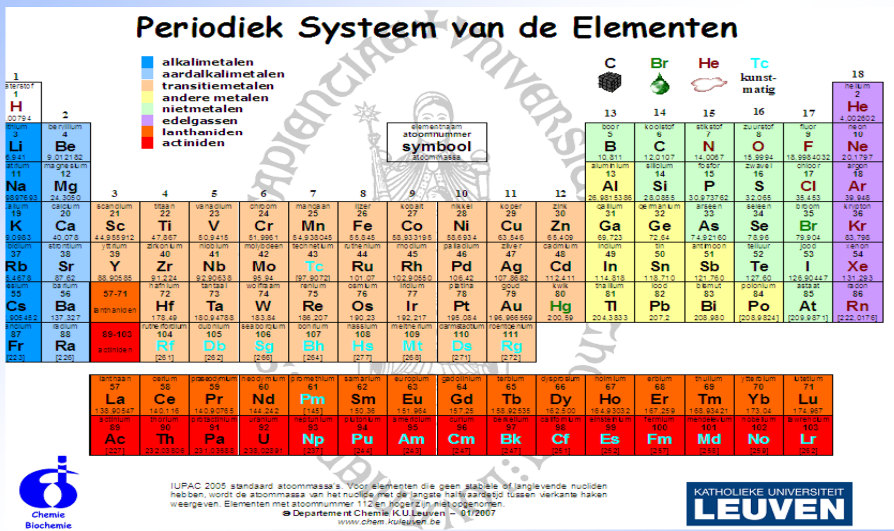
Waarom Li-ion?

- 

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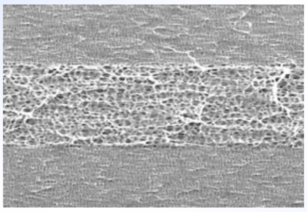
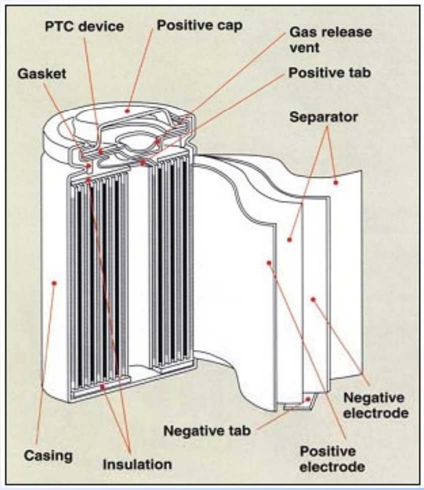
Batterijen

- Li-ion
- Separatiemembraan: bevat geen water ($2Li+2H_2O=H_2 +2LiOH$) + eventueel 
- Beste: 3 laag PP/PE/PP

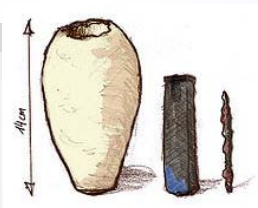




Een korte geschiedenis

- Baghdad batterij (rond Christus; acupunctuur?)

Year	Inventor	Activity
1600	William Gilbert (UK)	Establishment of electrochemistry study
1791	Luigi Galvani (Italy)	Discovery of “animal electricity”
1800	Alessandro Volta (Italy)	Invention of the voltaic cell (zinc, copper disks)
1802	William Cruickshank (UK)	First electric battery capable of mass production
1820	André-Marie Ampère (France)	Electricity through magnetism
1833	Michael Faraday (UK)	Announcement of Faraday’s law
1836	John F. Daniell (UK)	Invention of the Daniell cell
1839	William Robert Grove (UK)	Invention of the fuel cell (H_2/O_2)
1859	Gaston Planté (France)	Invention of the lead acid battery
1868	Georges Leclanché (France)	Invention of the Leclanché cell (carbon-zinc)
1899	Waldmar Jungner (Sweden)	Invention of the nickel-cadmium battery



Een korte geschiedenis

1901	Thomas A. Edison (USA)	Invention of the nickel-iron battery
1932	Shlecht & Ackermann (D)	Invention of the sintered pole plate
1947	Georg Neumann (Germany)	Successfully sealing the nickel-cadmium battery
1949	Lew Urry, Eveready Battery	Invention of the alkaline-manganese battery
1970s	Group effort	Development of valve-regulated lead acid battery
1990	Group effort	Commercialization of nickel-metal-hydride battery
1991	Sony (Japan)	Commercialization of lithium-ion battery
1994	Bellcore (USA)	Commercialization of lithium-ion polymer
1996	Moli Energy (Canada)	Introduction of Li-ion with manganese cathode
1996	University of Texas (USA)	Identification of Li-phosphate ($LiFePO_4$)
2002	University of Montreal, Quebec Hydro, MIT, others	Improvement of Li-phosphate, nanotechnology, commercialization

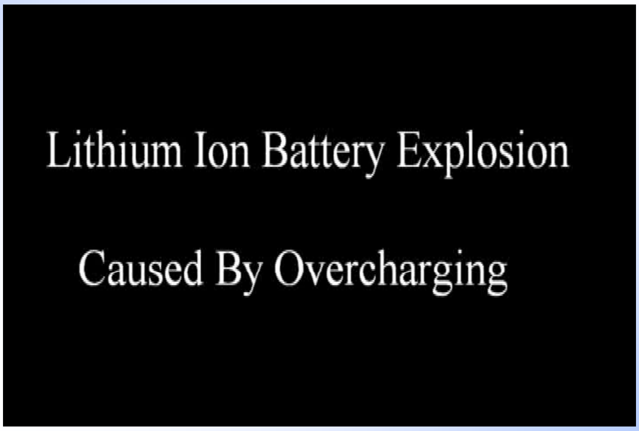
- Vergeten in tabel op http://batteryuniversity.com/learn/article/battery_developments
  Vloeibaar Natrium(zouten)/S (245° C)?
  Dr. Ing. Georg Otto Erb (V1-V2, later in atoomwapens)
  90 Wh/kg and a specific power of 150 W/kg

Waarom Li-ion?

- Studentenbatterij: 2 appelen, 1 banaan, 1 oranje, 2 citroenen (in serie)
- Zn + Cu elektrodes

Uitzonderlijke problemen

- Overladen/kortsluiten: veilig tot 50° C (omhulsel), … daarna brandbare witte rook (na ontploffing omhulsel).



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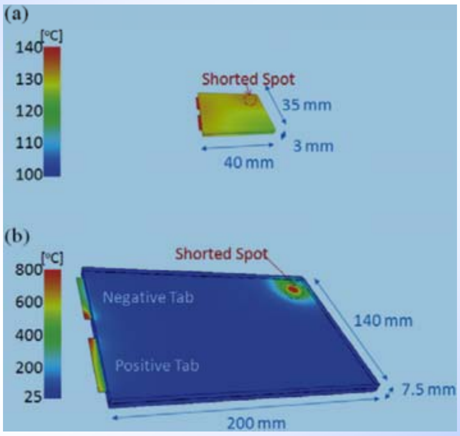
Uitzonderlijke problemen

- Lokale kortsluiting (te wijten aan losse Li deeltjes/dendrieten), of door inbrengen van nagel.



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Uitzonderlijke problemen

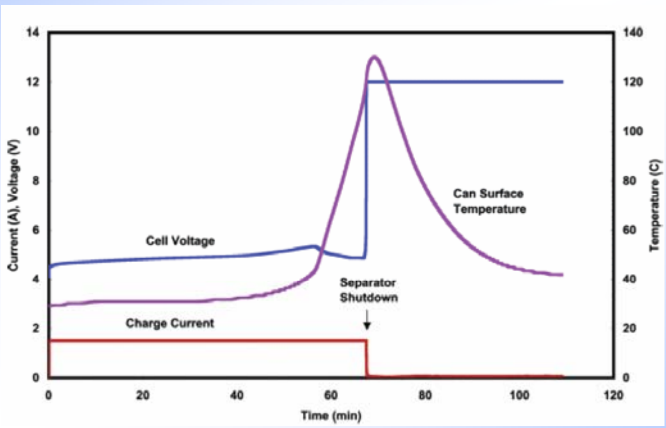
- Oplossingen:
  - meer lagen
    - PE heeft smelttemperatuur op 135° C en PP op 165° C.
    - PE smelt eerst en vult poriën van PP op: vermindert weerstand: → inherent stabiel
  - hogere temperaturen (ceramisch)

Table I. Commercial separator properties.*

	Entek	Exxon	Degussa	Celgard
Product	Teklon	Tonen	Separion	2325
Thickness (µm)	25	25	25	25
Single/multilayer	Single layer	Single layer	Trilayer	Trilayer
Composition	PE	PE	Ceramic-PET-Ceramic	PP-PE-PP
Process	Wet extruded	Wet extruded	Wet-laid mat	Dry extruded
Porosity (%)	38	36	>40	41
Melt temperature	135	135	220	134/166

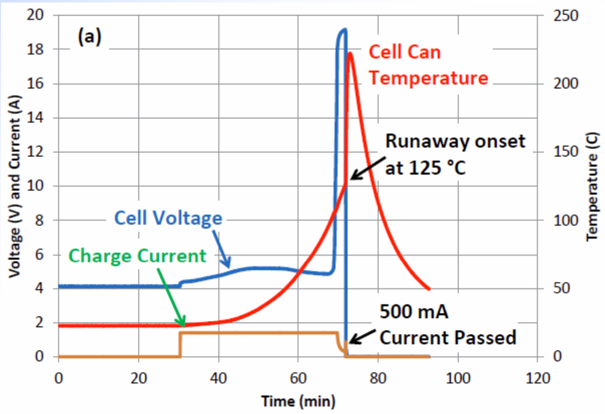
Uitzonderlijke problemen

- Verloop van ideale overlaadbeveiliging



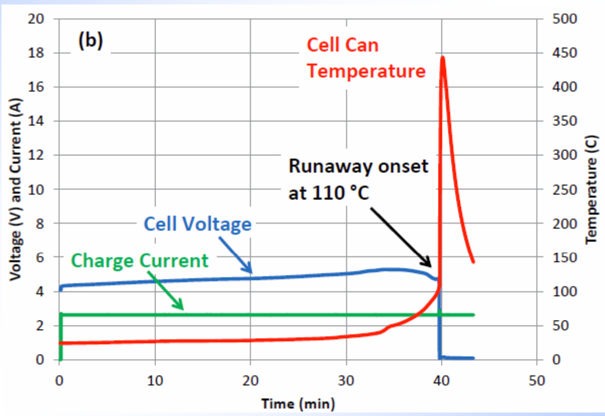
Uitzonderlijke problemen

- Verloop van werkelijke overlaadbeveiliging (met interne kortsluiting te wijten aan overspanning)



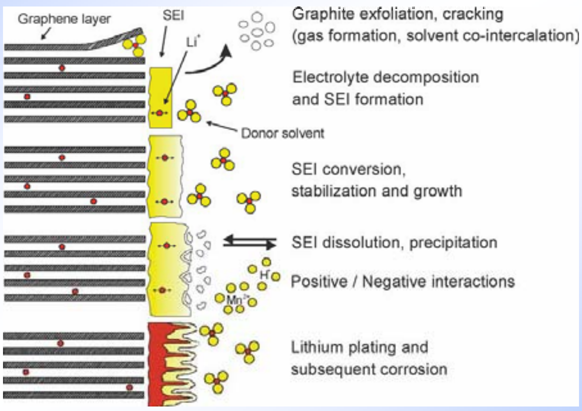
Uitzonderlijke problemen

- Verloop van werkelijke overlaadbeveiliging (met interne kortsluiting door te grote laadstroom (2(,5)x))



Verouderingsverschijnselen

- Aan de kant van de anode (inert grafiet)
- Beschermd door S(olid)E(lectrolite)I(interface)



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Verouderingsverschijnselen

Lithium-ion anode ageing—causes, effects, and influences

Cause	Effect	Leads to	Reduced by	Enhanced by
Electrolyte decomposition (→SEI) (Continuous side reaction at low rate)	Loss of lithium Impedance rise	**Capacity fade** **Power fade**	Stable SEI (additives) Rate decreases with time	High temperatures High SOC (low potential)
Solvent co-intercalation, gas evolution and subsequent cracking formation in particles	Loss of active material (graphite exfoliation) Loss of lithium	Capacity fade	Stable SEI (additives) Carbon pre-treatment	Overcharge
Decrease of accessible surface area due to continuous SEI growth	Impedance rise	**Power fade**	Stable SEI (additives)	High temperatures High SOC (low potential)
Changes in porosity due to volume changes, SEI formation and growth	Impedance rise Overpotentials	Power fade	External pressure Stable SEI (additives)	High cycling rate High SOC (low potential)

- SOC=State Of Charge

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Verouderingsverschijnselen

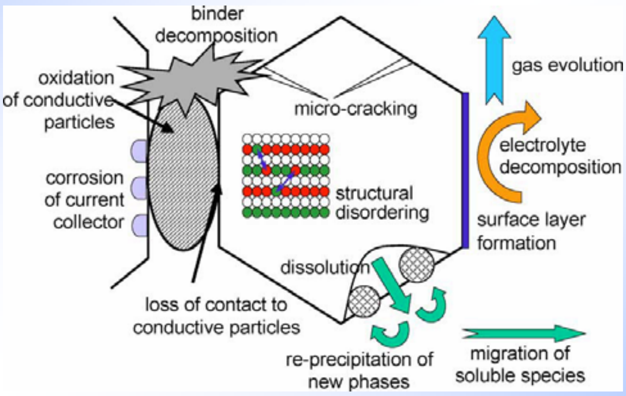
Lithium-ion anode ageing—causes, effects, and influences

Cause	Effect	Leads to	Reduced by	Enhanced by
Contact loss of active material particles due to volume changes during cycling	Loss of active material	**Capacity fade**	External pressure	High cycling rate High DOD
Decomposition of binder	Loss of lithium Loss of mechanical stability	Capacity fade	Proper binder choice	High SOC (low potential) High temperatures
Current collector corrosion	Overpotentials Impedance rise Inhomogeneous distribution of current and potential	Power fade Enhances other ageing mechanisms	Current collector pre-treatment (?)	Overdischarge Low SOC (high potential)
Metallic lithium plating and subsequent electrolyte decomposition by metallic Li	Loss of lithium (Loss of electrolyte)	Capacity fade (power fade)	Narrow potential window	Low temperature High cycling rates Poor cell balance Geometric misfits

- DOD=Depth Of Discharge

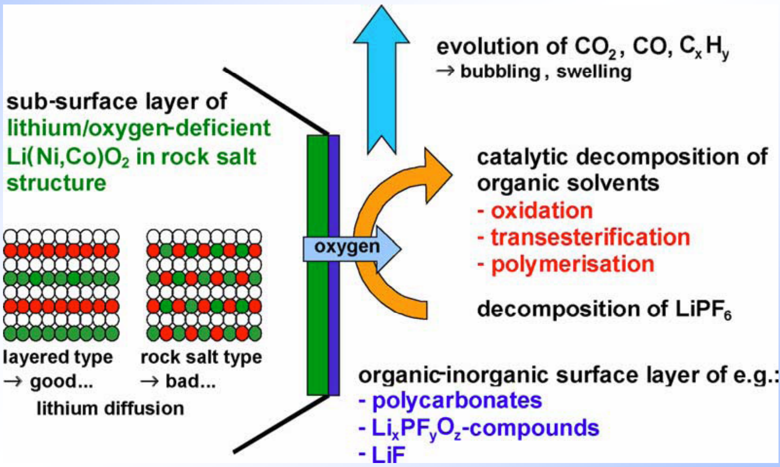
Verouderingsverschijnselen

- Aan de kant van de cathode
  - $LiMn_2O_4$ / $Li(Ni,Co)O_2$



Verouderingsverschijnselen

- Aan de kant van de cathode ($LiMeO_2$ in $LiPF_6$ electrolyt)



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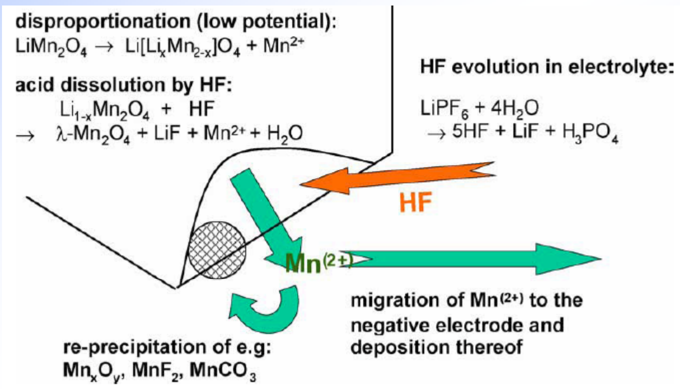
Verouderingsverschijnselen

- Aan de kant van de cathode ($LiMn_2O_4$ in LPF_6 electrolyt)



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Specifiek 787

- Volgens Prof. Adam Heller (U. of Texas, Austin)
- Dendrieten op anode
- Oplossing

  “The G. S. Yuasa-Boeing 787 Li-ion Battery:

  Test It at a Low Temperature and Keep It Warm in Flight”

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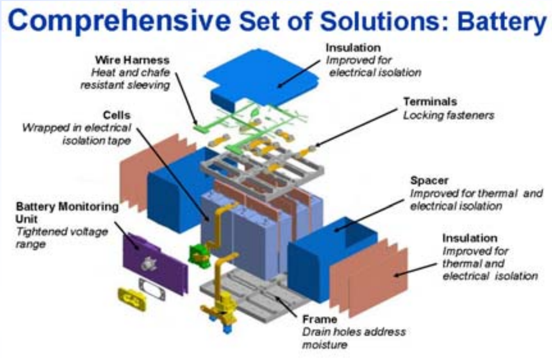
Oplossing Boeing voor 787

- Kleinere laadstroom
- Ontluchting/ontwatering: direct naar buiten (no “smoke in the cockpit”)
- Geen temperatuurscontrole, wel isolatie; propagatie van brand tegengaan
- Kost: 150 pond = 75 kg (kwijt wat door Li-ion gewonnen was)



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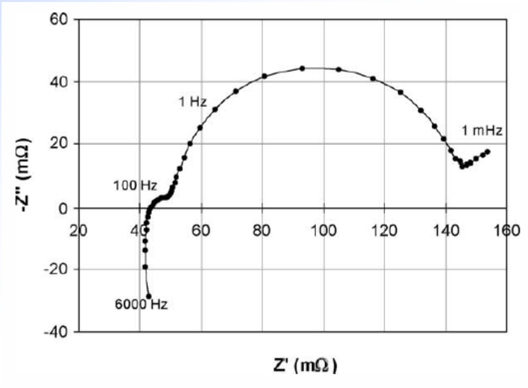
Impedantieverloop

- LF capacitief (-Z”!), vanaf ±1 kHz inductief.



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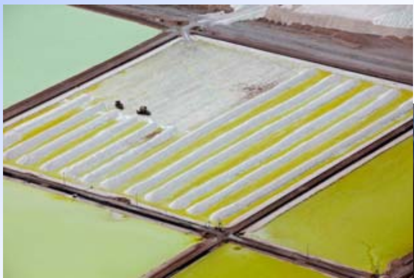
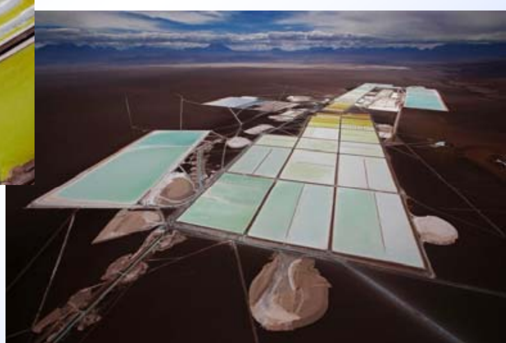
Waar te vinden?

- Chili (Soquimich) (40%; 44% import naar VS 2008-2011) (Australië = 2[de] grootste na Chili, China = 3[de])





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Waar te vinden?

- Salar del Hombre Muerto, N van Argentinië (44% import naar VS 2008-2011)

Waar te vinden?

- zoutmeer van Uyuni, 's werelds grootste lithiumvoorraad, ZW Bolivië (3656 m); pas sinds 2013 in exploitatie.

Referenties

- http://www.youtube.com/watch?v=SMy2_qNO2Y0
- http://www.youtube.com/watch?v=aNG-Q49mIbM met Duitse brandweer + IR camera (nagel erdoor kloppen + water opgieten)
- C. Orendorff, “The Role of Separators in Lithium-ion Cell Safety”, The Electrochemical Society, Interface, Vol. 21, no. 2, Summer 2012, Special Issue on “Lithium Ion Battery SAFETY”, pp.61-66
- J. Vetter e.a., “Ageing mechanisms in Lithium-ion batteries”, Journal of Power sources, 147, 2005, pp.269-281
- Artikel van Prof. Heller http://www.electrochem.org/dl/interface/sum/sum13/sum13_p035.pdf The Electrochemical Society, Interface, Vol. 22, no. 2, Summer 2013, Special Issue on “Solar Fuels”, p. 35

Vragen

- Commentaar!

Extra slides

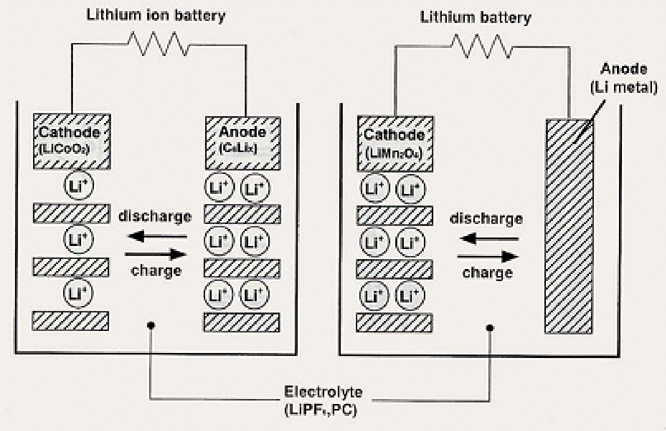

Fig. 1.5 Lithium metal and Lithium-ion batteries.